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(54) Title: AGGLOMERATION PROCESS FOR PRODUCING A PARTICULATE MODIFIER POLYAMINE DETERGENT ADMIX

(57) Abstract

A process is provided in which selected modified polyamines are agglomerated with a particulate carrier to provide a high active agglomerated detergent admix composition for incorporation into fully formulated detergent compositions. The detergent admix composition produced by the process has improved performance from both a cleaning and physical property standpoint.

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AGGLOMERATION PROCESS FOR PRODUCING A PARTICULATE MODIFIER POLYAMINE DETERGENT ADMIX

FIELD OF THE INVENTION

The present invention relates to an agglomeration process for producing laundry detergent admix composition in particulate form that contain modified polyamines especially useful as cotton soil release and/or dispersant agents. More specifically, the process involves agglomerating a modified polyamine with a particulate carrier in one or more mixer/densifiers so as to provide the desired particulate detergent admix.

BACKGROUND OF THE INVENTION

Various fabric surface modifying agents have been commercialized and are currently used in detergent compositions and fabric softener/antistatic articles and compositions. Examples of surface modifying agents are soil release polymers. Soil release polymers typically comprise an oligomeric or polymeric ester "backbone" and are generally very effective on polyester or other synthetic fabrics where the grease or similar hydrophobic stains form an attached film and are not easily removed in an aqueous laundering process. The soil release polymers have a less dramatic effect on "blended" fabrics, that is, on fabrics that comprise a mixture of cotton and synthetic material, and have little or no effect on cotton articles.

Extensive research in this area has yielded significant improvements in the effectiveness of polyester soil release agents yielding materials with enhanced product performance and capability of being incorporated into detergent formulations. Modifications of the polymer backbone as well as the selection of proper end-capping groups have produced a wide variety of polyester soil release polymers. For example, end-cap modifications, such as the use of sulfoaryl moieties and especially the low cost isethionate-derived end-capping units, have increased the range of solubility and adjunct ingredient compatibility of these polymers without sacrifice to soil release effectiveness. Many polyester soil release polymers can now be formulated into both liquid as well as solid (i.e., granular) detergents.

As in the case of polyester soil release agents, producing an oligomeric or polymeric material that mimics the structure of cotton has not resulted in a cotton soil release polymer. Although cotton and polyester fabric are both comprised of long chain polymeric materials, they are chemically very different. Cotton is comprised of cellulose fibers that consist of anhydroglucose units joined by 1-4 linkages. These glycosidic linkages characterize the cotton cellulose as a

polysaccharide whereas polyester soil release polymers are generally a combination of terephthalate and ethylene/propylene oxide residues. These differences in composition account for the difference in the fabric properties of cotton versus polyester fabric. Cotton is hydrophilic relative to polyester. Polyester is hydrophobic and attracts oily or greasy dirt and can be easily "dry cleaned". Importantly, the terephthalate and ethyleneoxy/propyleneoxy backbone of polyester fabric does not contain reactive sites, such as the hydroxyl moieties of cotton, that react with stains in a different manner than synthetics. Many cotton stains become "fixed" and can only be resolved by bleaching the fabric.

Until recently, the developm nt of effective fabric surface modifying agents for use on cotton fabrics has been elusive. Attempts by others to apply the paradigm of matching the structure of a soil release polymer with the structure of the fabric, a method successful in the polyester soil release polymer field, have nevertheless yielded marginal results when applied to other fabric surface modifying agents, especially for cotton fabrics. For example, the use of methylcellulose, a cotton polysaccharide with modified oligomeric units, proved to be more effective on polyesters than on cotton.

Additionally, detergent formulators have been faced with the task of devising products to remove a broad spectrum of soils and stains from fabrics. The varieties of soils and stains ranges within a spectrum spanning from polar soils, such as proteinaceous, clay, and inorganic soils, to non-polar soils, such as soot, carbon-black, by- products of incomplete hydrocarbon combustion, and organic soils. To that end, detergent compositions have become more complex as formulators attempt to provide products which handle all types of such soils concurrently. Formulators have been highly successful in developing traditional dispersants which are particularly useful in suspending polar, highly charged, hydrophilic particles such as clay. As yet, however, dispersants designed to disperse and suspend non-polar, hydrophobic-type soils and particulates have been more difficult to develop.

It has been discovered that effective soil release agents for cotton articles and dispersants can be prepared from certain modified polyamines. This has yielded compositions that are key to providing these benefits once available to only synthetic and synthetic-cotton blended fabric. However, the manner in which such modified polyamines may be included into fully formulated detergent compositions so as to retain, and preferably, improve performance has remained unresolved. In fact, the modified polyamines described herein typically are extremely viscous liquids or waxy solids which cannot be advantageously sprayed onto granular detergent compositions. Moreover, these modified polyamines are usually highly viscous and

yellow or otherwise not clear in color which in turn, discolors and causing caking of the detergent composition onto which it is sprayed. Consumers have a strong preference for non-caked (i.e., easy to scoop or dispense from the product container), pure colored (e.g., white or white with discrete colored speckles) granular detergent products. Additionally, these modified polyamines are odorous which can have deleterious effects on the final product odor.

Accordingly, there remains a need in the art for a process which produces selected modified polyamines in a form suitable for incorporation into fully formulated granular detergent compositions. In doing this, there remains a need for the granular detergent composition into which the modified polyamines are incorporated which retains the desired, odor, color and physical properties.

BACKGROUND ART

U.K. 1,314,897, published April 26, 1973 teaches a hydroxypropyl methyl cellulose material for the prevention of wet-soil redeposition and improving stain release on laundered fabric. U. S. Patent No. 3,897,026 issued to Kearney, discloses cellulosic textile materials having improved soil release and stain resistance properties obtained by reaction of an ethylene-maleic anhydride co-polymer with the hydroxyl moieties of the cotton polymers. U.S. Patent No. 3,912,681 issued to Dickson teaches a composition for applying a non-permanent soil release finish comprising a polycarboxylate polymer to a cotton fabric. U.S. Patent No. 3,948,838 issued to Hinton, *et alia* describes high molecular weight (500,000 to 1,500,000) polyacrylic polymers for soil release. U.S. Patent 4,559,056 issued to Leigh, *et alia* discloses a process for treating cotton or synthetic fabrics with a composition comprising an organopolysiloxane elastomer, an organosiloxaneoxyalkylene copolymer crosslinking agent and a siloxane curing catalyst. See also U.S. Patent Nos. 4,579,681 and 4,614,519. These disclose vinyl caprolactam materials have their effectiveness limited to polyester fabrics, blends of cotton and polyester, and cotton fabrics rendered hydrophobic by finishing agents.

In addition to the above cited art, the following disclose various soil release polymers or modified polyamines; U.S. Patent 4,548,744, Connor, issued October 22, 1985; U.S. Patent 4,597,898, Vander Meer, issued July 1, 1986; U.S. Patent 4,877,896, Maldonado, et al., issued October 31, 1989; U.S. Patent 4,891,160, Vander Meer, issued January 2, 1990; U.S. Patent 4,976,879, Maldonado, et al., issued December 11, 1990; U.S. Patent 5,415,807, Gosselink, issued May 16,1995; U.S. Patent 4,235,735, Marco, et al., issued November 25, 1980; U.K. Patent 1,537,288, published December 29, 1978; U.K. Patent 1,498,520, published January 18, 1978; WO 95/32272, published November 30, 1995; European Patent

Application 206,513; German Patent DE 28 29 022, issued January 10, 1980; Japanese Kokai JP 06313271, published April 27, 1994.

The following references are directed to densifying spray-dried granules: Appel et al, U.S. Patent No. 5,133,924 (Lever); Bortolotti et al, U.S. Patent No. 5,160,657 (Lever); Johnson et al, British patent No. 1,517,713 (Unilever); and Curtis, European Patent Application 451,894. The following references are directed to producing detergents by agglomeration: Capeci et al, U.S. Patent 5,366,652, issued November 22, 1994 and Capeci et al, U.S. Patent 5,486,303, issued January 23, 1996; Beerse et al, U.S. Patent No. 5,108,646 (Procter & Gamble); Hollingsworth et al, European Patent Application 351,937 (Unilever); and Swatling et al, U.S. Patent No. 5,205,958.

SUMMARY OF THE INVENTION

The aforementioned needs in the art are met by the present invention which provides a process in which selected modified polyamines are agglomerated with a particulate carrier to form high active agglomerates for incorporation into fully formulated detergent compositions. The process provides a particulate detergent admix containing selected modified polyamines that unexpectedly exhibit enhanced dispersancy and cleaning performance, especially relative to cotton-containing fabrics. By use of the instant process, the need for spraying on or otherwise incorporating the selected modified polyamines is eliminated resulting in a fully formulated detergent product which is not discolored and has improved cleaning performance.

In accordance with one aspect of the invention, a process for an agglomerated detergent composition is provided. The process comprises the step of agglomerating from about 20% to about 90% by weight of a particulate carrier with from about 10% to about 80% by weight of a water-soluble or dispersible, modified polyamine in a mixer so as to form agglomerates containing said particulate carrier and said modified polyamine, thereby forming said agglomerated detergent admix, said modified polyamine having a polyamine backbone corresponding to the formula:

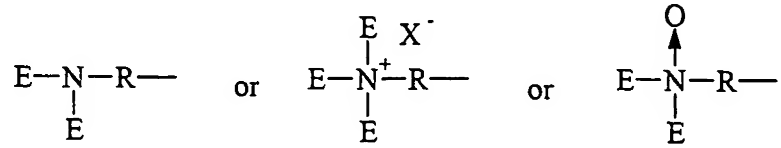
$$[H_2N-R]_{n+1}-[\overset{H}{\overset{|}{N}}-R]_m-[\overset{|}{N}-R]_n-NH_2$$

having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:

$$[H_2N-R]_{n-k+1}-[\overset{H}{\overset{|}{N}}-R]_m-[\overset{|}{N}-R]_n-[\overset{\overset{|}{R}}{\overset{|}{N}}-R]_k-NH_2$$

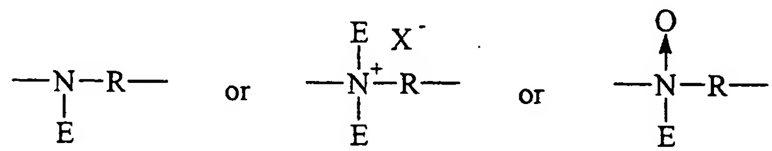
having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n, said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

i) V units are terminal units having the formula:



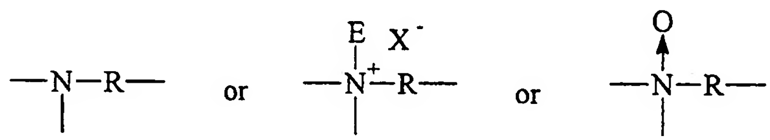
;

ii) W units are backbone units having the formula:



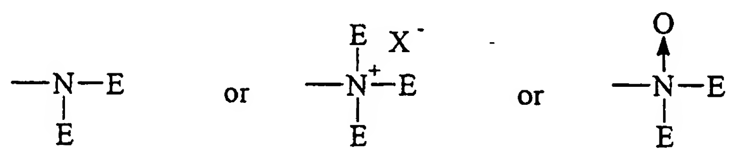
;

iii) Y units are branching units having the formula:



; and

iv) Z units are terminal units having the formula:



;

wherein backbone linking R units are selected from the group consisting of C_2-C_{12} alkylene, C_4-C_{12} alkenylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxy-alkylene, C_8-C_{12} dialkylarylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OR^2)CH_2-$, and mixtures thereof; wherein R^1 is C_2-C_6 alkylene and mixtures thereof; R^2 is hydrogen, $-(R^1O)_xB$, and mixtures thereof; R^3 is C_1-C_{18} alkyl, C_7-C_{12} arylalkyl, C_7-C_{12} alkyl substituted aryl, C_6-C_{12} aryl, and mixtures thereof; R^4 is C_1-C_{12} alkylene, C_4-C_{12} alkenylene, C_8-C_{12} arylalkylene, C_6-C_{10} arylene, and mixtures thereof; R^5 is C_1-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxy-alkylene, C_8-C_{12} dialkylarylene, $-C(O)-$, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, and mixtures thereof; R^6 is C_2-C_{12} alkylene or C_6-C_{12} arylene; E units are selected from the group consisting of

hydrogen, C_1-C_{22} alkyl, C_3-C_{22} alkenyl, C_7-C_{22} arylalkyl, C_2-C_{22} hydroxy-alkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_xB$, $-C(O)R^3$, and mixtures thereof; oxide; B is hydrogen, C_1-C_6 alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q-(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1. Also provided by the invention are the detergent compositions made by any of the processes described herein.

As used herein, the term "agglomerates" refers to particles formed by agglomerating detergent granules or particles which typically have a smaller median particle size than the formed agglomerates. All documents cited herein are incorporated by reference, and all percentages used herein are expressed as "percent-by-weight" unless indicated otherwise. Accordingly, it is an object of the invention to provide a process for producing an agglomerated detergent admix composition which provides a means by which selected modified polyamines can be incorporated into fully formulated detergent compositions without deleterious affecting its (physical properties and improving) cleaning performance and physical properties. These and other objects, features and attendant advantages of the present invention will become apparent to those skilled in the art from a reading of the following detailed description of the preferred embodiment and the appended claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The process of the instant invention involves agglomerating selected modified polyamines and a particulate carrier to form a highly active particulate detergent admix. It has been found that the problems associated with incorporating selected modified polyamines as described more fully hereinafter directly into granular detergent compositions are solved by the process. In particular, the highly viscous nature of selected modified polyamines and their inevitable deleterious effect on the physical properties of the detergent product onto which they are sprayed are ameliorated by including the polyamines in a high active agglomerated particle. The present invention provides a suitable process for incorporating such modified polyamines at suitable active levels into a granular detergent admix having acceptable color (e.g., not excessive yellow), causing odor and physical properties. The present process achieves this goal by using an agglomeration step with selected amounts of the modified polyamine and a particulate carrier to provide a high active

particle which enhances the cleaning performance of the detergent composition as compared to compositions not containing such modified polyamines.

Preferably, the process employs from about 10% to about 80%, more preferably from about 20% to about 65%, and most preferably from about 25% to about 50% by weight of the modified polyamine. The particulate carrier is present in an amount of from about 20% to about 90%, more preferably from about 35% to about 80%, and most preferably from about 50% to about 75% by weight. The particulate carrier can be any particulate material capable of holding or otherwise carrying the modified polyamines described herein that is suitable for use in detergent compositions. Conveniently, the carrier can be particulate detergent materials traditionally used as a detergency builder or filler in fully formulated detergent compositions. Preferably, the particulate carrier is selected from the group consisting of aluminosilicates, phosphates, sulfates, carbonates, silicas and mixtures thereof. Other preferable embodiments entail having the particulate carrier to be a mixture of sodium carbonate, sodium tripolyphosphate, and aluminosilicate. Most preferably, the particulate carrier is aluminosilicate which is discussed in U.S. Patent No. 3,985,669 to Krummel et al or a precipitated silica, such as Sipernat 22 commercially available from DeGussa. This and the other suitable particulate carriers are discussed in U.S. Patent No. 5,658,867 to Pancheri et al. It has also been found that it is beneficial for the viscosity of the modified polyamine to be from about 100 cps to about 5000 cps at a temperature of from about 4°C to about 50°C. This enhances adequate agglomeration in the current process.

The agglomeration step of the process preferably occurs in a conventional mixer including but not limited to a Lödige CB or KM mixer, Schugi or similar brand mixer. The Lödige type of mixers essentially consist of a horizontal, hollow static cylinder having a centrally mounted rotating shaft around which several plough-shaped blades are attached. Preferably, in these types of mixers, the shaft rotates at a speed of from about 200 rpm to about 4000 rpm, more preferably from about 300 rpm to about 1600 rpm. Preferably, the mean residence time of the detergent ingredients in the mixer is preferably in range from about 1 second to about 20 minutes, and most preferably from about 0.5 minutes to about 15 minutes. The particular time will largely depend on the process equipment and nature of the process (i.e., batch or continuous). The present process typically provides agglomerates having a median particle size of from about 400 microns to about 700 microns, and more preferably from about 400 microns to about 600 microns. As used herein, the phrase "median particle size" refers to individual agglomerates and not individual particles or detergent granules.

Optionally, other mixers can be used in series with the first mixer if additional agglomeration is desired and/or solvents can be added to one or more of the mixers to enhance agglomeration. In another optional step of the present process, the agglomerates formed by the process are dried in a fluid bed dryer and/or further conditioned by cooling the agglomerates in a fluid bed cooler or similar apparatus as are well known in the art. Other optional steps in the present process involve recycling oversized and undersized agglomerates as described in Capeci et al, U.S. Patent Nos. 5,489,392 and 5,516,448 (Procter & Gamble).

Modified Polyamines

The modified polyamines used in the process invention are water-soluble or dispersible, especially useful for cleaning cotton-containing fabrics or as a dispersant. These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also comprise polyamine branching chains to a greater or lesser degree. In general, the polyamine backbones described herein are modified in such a manner that each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

For the purposes of the present invention the term "modification" is defined as replacing a backbone -NH hydrogen atom by an E unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an E unit. Quaternization or oxidation may take place in some circumstances without substitution, but preferably substitution is accompanied by oxidation or quaternization of at least one backbone nitrogen.

The linear or non-cyclic polyamine backbones that comprise the polymers used in the process have the general formula:

$$[H_2N-R]_{n+1}-[\overset{\displaystyle H}{\overset{|}{N}}-R]_m-[\overset{|}{N}-R]_n-NH_2$$

said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units. The cyclic polyamine backbones have the general formula:

$$[H_2N-R]_{n-k+1}-[\overset{\displaystyle H}{\overset{|}{N}}-R]_m-[\overset{|}{N}-R]_n-[\overset{\overset{|}{\displaystyle R}}{\overset{|}{N}}-R]_k-NH_2$$

said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units

For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure

$$H_2N\text{-}R]\text{-}$$

is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure

$$\text{-}NH_2$$

is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure

$$\text{—}[\overset{\displaystyle H}{\overset{|}{N}}\text{-}R]\text{—}$$

is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure

$$\text{—}[\overset{|}{N}\text{-}R]\text{—}$$

is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all or the tertiary amine moieties can remain unmodified. These

unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

The final modified structure of the polyamines of the present invention can be therefore represented by the general formula

$$V_{(n+1)}W_mY_nZ$$

for linear polyamines, by the general formula

$$V_{(n-k+1)}W_mY_nY'_kZ$$

for cyclic polyamine polymers. For the case of polyamines comprising rings, a Y' unit of the formula

$$\begin{array}{c} | \\ R \\ | \\ -[N-R]- \end{array}$$

serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula

$$\begin{array}{c} | \\ -[N-R]- \end{array}$$

that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula

$$[H_2N-R]_n-\overset{\displaystyle H}{\overset{|}{[N}}-R]_m-\overset{|}{[N}-R]_n-$$

therefore comprising no Z terminal unit and having the formula

$$V_{n-k}W_mY_nY'_k$$

wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula

$$VW_mZ$$

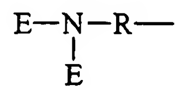
that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 4 to about 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of

one of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

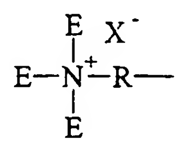
Modified primary amine moieties are defined as V "terminal" units having one of three forms:

a) simple substituted units having the structure:



,

b) quaternized units having the structure:



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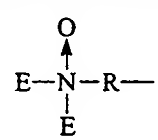
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:



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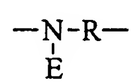
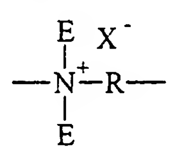
Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

a) simple substituted units having the structure:



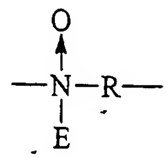
,

b) quaternized units having the structure:



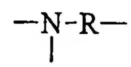
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

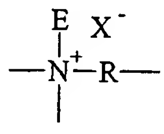


Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

a) unmodified units having the structure:

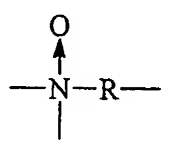


b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

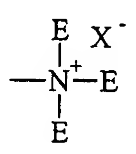
c) oxidized units having the structure:



Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

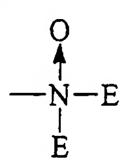
a) simple substituted units having the structure:

b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:



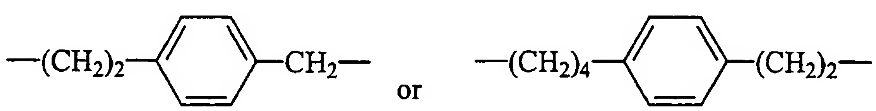
When any position on a nitrogen is unsubstituted of unmodified, it is understood that hydrogen will substitute for E. For example, a primary amine unit

comprising one E unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula

$(HOCH_2CH_2)HN$-.

For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure $-NH_2$. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the E units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore E cannot be a hydrogen.

The polyamines of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C_2-C_{12} alkylene, C_4-C_{12} alkenylene, C_3-C_{12} hydroxyalkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C_4-C_{12} dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; C_8-C_{12} dialkylarylene which for the purpose of the present invention are arylene moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula



although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted C_2-C_{12} alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise $-(R^1O)_xR^5(OR^1)_x-$, $-CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w-$, $-CH_2CH(OR^2)CH_2-$, $-(R^1O)_xR^1-$, and mixtures thereof. Preferred R units are C_2-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_8-C_{12} dialkylarylene, $-(R^1O)_xR^1-$, $-CH_2CH(OR^2)CH_2-$, $-(CH_2CH(OH)CH_2O)_z(R^1O)_yR^1(OCH_2CH-(OH)CH_2)_w-$, $-(R^1O)_xR^5(OR^1)_x-$, more preferred R units are C_2-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OH)CH_2O)_z(R^1O)_yR^1(OCH_2CH-(OH)CH_2)_w-$, and mixtures thereof, even more preferred R units are C_2-C_{12} alkylene, C_3 hydroxyalkylene, and mixtures

thereof, most preferred are C_2-C_6 alkylene. The most preferred backbones of the present invention comprise at least 50% R units that are ethylene.

R^1 units are C_2-C_6 alkylene, and mixtures thereof, preferably ethylene. R^2 is hydrogen, and $-(R^1O)_xB$, preferably hydrogen.

R^3 is C_1-C_{18} alkyl, C_7-C_{12} arylalkylene, C_7-C_{12} alkyl substituted aryl, C_6-C_{12} aryl, and mixtures thereof , preferably C_1-C_{12} alkyl, C_7-C_{12} arylalkylene, more preferably C_1-C_{12} alkyl, most preferably methyl. R^3 units serve as part of E units described herein below.

R^4 is C_1-C_{12} alkylene, C_4-C_{12} alkenylene, C_8-C_{12} arylalkylene, C_6-C_{10} arylene, preferably C_1-C_{10} alkylene, C_8-C_{12} arylalkylene, more preferably C_2-C_8 alkylene, most preferably ethylene or butylene.

R^5 is C_1-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_8-C_{12} dialkylarylene, -C(O)-, $-C(O)NHR^6NHC(O)-$, -$C(O)(R^4)_rC(O)-$,

$-R^1(OR^1)-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, R^5 is preferably ethylene, -C(O)-, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH$-$(OH)CH_2-$, more preferably $-CH_2CH(OH)CH_2-$.

R^6 is C_2-C_{12} alkylene or C_6-C_{12} arylene.

The preferred "oxy" R units are further defined in terms of the R^1, R^2, and R^5 units. Preferred "oxy" R units comprise the preferred R^1, R^2, and R^5 units. The preferred modified polyamines comprise at least 50% R^1 units that are ethylene. Preferred R^1, R^2, and R^5 units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

i) Substituting more preferred R^5 into $-(CH_2CH_2O)_xR^5(OCH_2CH_2)_x-$ yields $-(CH_2CH_2O)_xCH_2CHOHCH_2(OCH_2CH_2)_x-$.

ii) Substituting preferred R^1 and R^2 into $-(CH_2CH(OR^2)CH_2O)_z-(R^1O)_yR^1O(CH_2CH(OR^2)CH_2)_w-$ yields $-(CH_2CH(OH)CH_2O)_z-(CH_2CH_2O)_yCH_2CH_2O(CH_2CH(OH)CH_2)_w-$.

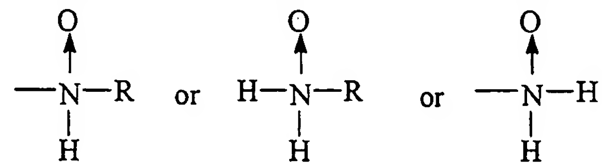
iii) Substituting preferred R^2 into $-CH_2CH(OR^2)CH_2-$ yields $-CH_2CH(OH)CH_2-$.

E units are selected from the group consisting of hydrogen, C_1-C_{22} alkyl, C_3-C_{22} alkenyl, C_7-C_{22} arylalkyl, C_2-C_{22} hydroxyalkyl, $-(CH_2)_pCO_2M$, -$(CH_2)_qSO_3M$,

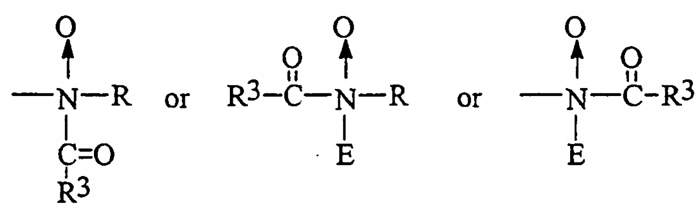
$-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_mB$, $-C(O)R^3$, preferably hydrogen, C_2-C_{22} hydroxyalkylene, benzyl, C_1-C_{22} alkylene, $-(R^1O)_mB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$,

$-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, more preferably C_1-C_{22} alkylene, -$(R^1O)_xB$,
$-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$,.$-CH(CH_2CO_2M)CO_2M$, most preferably C_1-C_{22} alkylene, $-(R^1O)_xB$, and $-C(O)R^3$. When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing E.

E units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



Additionally, E units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According to the present invention, the E unit $-C(O)R^3$ moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides having the structure



or combinations thereof.

B is hydrogen, C_1-C_6 alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q$-$(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, preferably hydrogen, $-(CH_2)_qSO_3M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q$-$(CHSO_2M)CH_2SO_3M$, more preferably hydrogen or $-(CH_2)_qSO_3M$.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies $-(CH_2)_pCO_2M$, and $-(CH_2)_qSO_3M$, thereby resulting in $-(CH_2)_pCO_2Na$, and $-(CH_2)_qSO_3Na$ moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required 516
chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a $-(CH_2)_pPO_3M$ moiety substituted with sodium atoms has the formula -

$(CH_2)_pPO_3Na_3$. Divalent cations such as calcium (Ca^{2+}) or magnesium (Mg^{2+}) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

X is a water soluble anion such as chlorine (Cl^-), bromine (Br^-) and iodine (I^-) or X can be any negatively charged radical such as sulfate (SO_4^{2-}) and methosulfate ($CH_3SO_3^-$).

The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; k is less than or equal to the value of n; m has the value from 4 to about 400, n has the value from 0 to about 200; m + n has the value of at least 5.

The preferred modified polyamines comprise polyamine backbones wherein less than about 50% of the R groups comprise "oxy" R units, preferably less than about 20% , more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

The most preferred polyamines which comprise no "oxy" R units comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C_2-C_{12} alkylene, preferred is C_2-C_3 alkylene, most preferred is ethylene.

The polyamines of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone. The proper manipulation of these "R unit chain lengths" provides the formulator with the ability to modify the solubility and fabric substantivity of the modified polymers.

Preferred polyamines of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's), or PEA's or PEI's connected by moieties having longer R units than the parent PAA's, PAI's, PEA's or PEI's. A common polyalkyleneamine (PAA) is tetrabutylenepentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and teraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Preferred amine polymer backbones comprise R units that are C_2 alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of about 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:

$$[H_2NCH_2CH_2]_n-[\overset{H}{N}CH_2CH_2]_m-[\overset{|}{N}CH_2CH_2]_n-NH_2$$

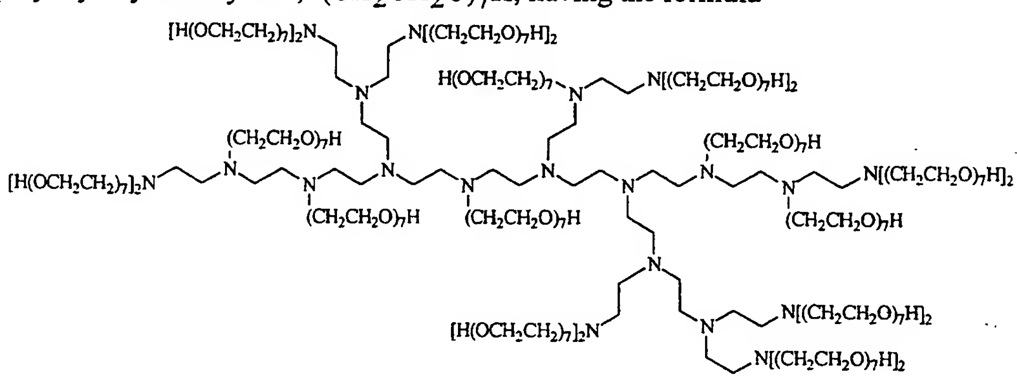
wherein m and n are the same as defined herein above. Preferred PEI's, prior to modification, will have a molecular weight greater than about 200 daltons.

The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

Examples of modified polyamines of the present invention comprising PEI's, are illustrated in Formulas I - IV:

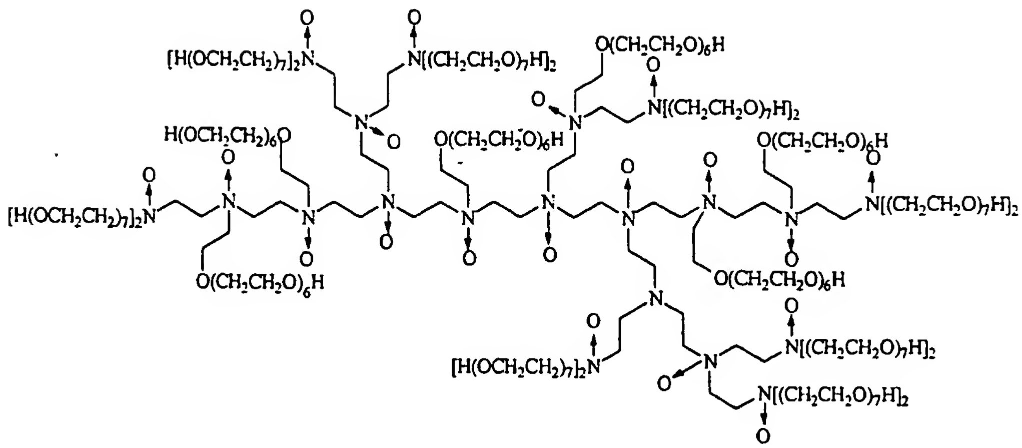
Formula I depicts a polymer comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_7H$, having the formula



Formula I

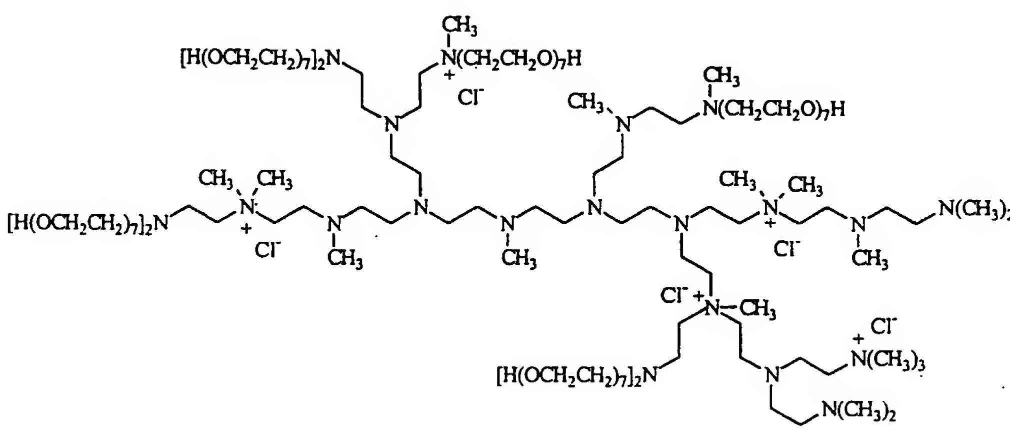
This is an example of a polymer that is fully modified by one type of moiety.

Formula II depicts a polymer comprising a PEI backbone wherein all substitutable primary amine nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_7H$, the molecule is then modified by subsequent oxidation of all oxidizable primary and secondary nitrogens to N-oxides, said polymer having the formula



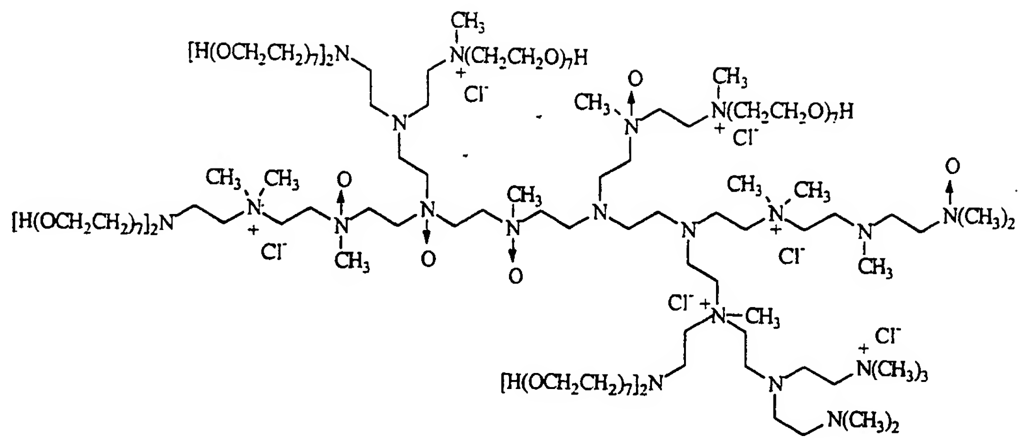
Formula II

Formula III depicts a polymer comprising a PEI backbone wherein all backbone hydrogen atoms are substituted and some backbone amine units are quaternized. The substituents are polyoxyalkyleneoxy units, $-(CH_2CH_2O)_7H$, or methyl groups. The modified PEI polymer has the formula



Formula III

Formula IV depicts a polymer comprising a PEI backbone wherein the backbone nitrogens are modified by substitution (i.e. by $-(CH_2CH_2O)_7H$ or methyl), quaternized, oxidized to N-oxides or combinations thereof. The resulting polymer has the formula



Formula IV

In the above examples, not all nitrogens of a unit class comprise the same modification. The present invention allows the formulator to have a portion of the secondary amine nitrogens ethoxylated while having other secondary amine nitrogens oxidized to N-oxides. This also applies to the primary amine nitrogens, in that the formulator may choose to modify all or a portion of the primary amine nitrogens with one or more substituents prior to oxidation or quaternization. Any possible combination of E groups can be substituted on the primary and secondary amine nitrogens, except for the restrictions described herein above.

In order to make the present invention more readily understood, reference is made to the following examples, which are intended to be illustrative only and not intended to be limiting in scope.

EXAMPLE I

Preparation of PEI 1800 E_7

This Example illustrates a method by which one of the selected modified polyamines is made. The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (Nippon Shokubai, Epomin SP-018 having a listed average molecular weight of 1800 equating to about 0.417 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while

cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen. In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

EXAMPLES II-XIII

A modified polyamine is made in accordance with Example I ("PEI1800 E7") or by method similar to Example I except that the molecular weight and degree of ethoxylation is altered to the desired level (e.g., "PEI3000 E30" or "PEI600 E20") and used in the process of the current invention to form an agglomerated detergent admix composition. A Lödige KM ("A"), Braun Model KSM2 household bean grinder ("B"), Braun Multiprac 280 Food Processor ("C"), or Hobart Ultra Power Blender Model KSM90 ("D") is used as a mixer into which the modified polyamine is added continuously along with a mixture of selected ingredients from the list including sodium aluminosilicate (zeolite), sodium tripolyphosphate, silica (e.g., Sipernat 22 from DeGussa), sodium sulfate, minor amounts of surfactants (e.g., linear alkylbenzene sulfonates and alkyl sulfates) and sodium carbonate. The resulting product is in the form of agglomerates which are screened with conventional screening apparatus resulting in a uniform particle size distribution. The compositions of the agglomerates exiting the mixer after screening and sizing are set forth in Table I below:

	% Weight				
Component	**II**	**III**	**IV**	**V**	**VI**
Sodium tripoly-phosphate	--	49.0	--	48.0	--
Sodium aluminosilicate	9.0	2.0	--	4.0	--
Sodium carbonate	73.0	29.0	--	28.0	--
Silica (Sipernat)	--	--	40.0	2.0	31.0
PEI1800 E7	18.0	20.0	60.0	18.0	13.0
PEI3000 E30	--	--	--	--	--
PEI600 E20	--	--	--	--	--
C_{12-15} alkyl ethoxy sulfate (EO3)	--	--	--	--	39.0
C_{12-15} linear alkyl-benzene sulfonate	--	--	--	--	--
Misc. (water)	--	--	--	--	17.0
Total	100.0	100.0	100.0	100.0	100.0
Mixer	B	D	B	A	C

Component	VII	VIII	IX	X	XI	XII	% Weight XIII
Sodium tripoly-phosphate	--	--	--	--	--	--	--
Sodium sulfate	--	--	--	--	--	--	24.0
Sodium alumino-silicate	--	--	72.0	72.0	71.0	71.0	47.0
Sodium carbonate	--	74.0	--	--	--	--	--
Silica (Sipernat)	35.0	--	2.0	3.0	3.0	3.0	6.0
PEI1800 E7	65.0	26.0	--	--	--	--	--
PEI3000 E30	--	--	26.0	--	24.0	--	--
PEI600 E20	--	--	--	25.0	--	23.0	23.0
C_{12-15} alkyl ethoxy sulfate (EO3)	--	--	--	--	--	--	--
C_{12-15} linear alkyl-benzene sulfonate	--	--	--	--	1.0	2.0	--
Misc. (water)	--	--	--	--	1.0	1.0	--
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Mixer	C	C	C	C	C	C	C

Having thus described the invention in detail, it will be clear to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

WHAT IS CLAIMED IS:

1. A process for producing an agglomerated detergent admix characterized by the step of:

agglomerating from 10% to 80% by weight of a particulate carrier with from 20% to 90% by weight of a water-soluble or dispersible, modified polyamine in a mixer so as to form agglomerates containing said particulate carrier and said modified polyamine, thereby forming said agglomerated detergent admix, said modified polyamine having a polyamine backbone corresponding to the formula:

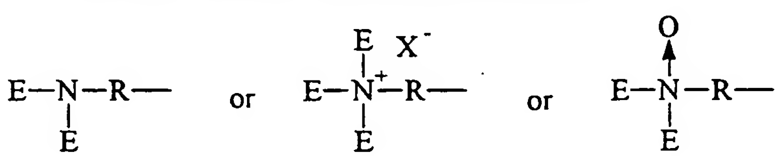
$$[H_2N-R]_{n+1}-[\overset{H}{\overset{|}{N}}-R]_m-[\overset{|}{N}-R]_n-NH_2$$

having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:

$$[H_2N-R]_{n-k+1}-[\overset{H}{\overset{|}{N}}-R]_m-[\overset{|}{N}-R]_n-[\overset{\overset{|}{R}}{\overset{|}{N}}-R]_k-NH_2$$

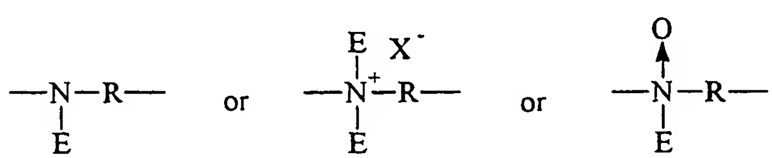
having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n, said polyamine backbone prior to modification has a molecular weight greater than 200 daltons, wherein

i) V units are terminal units having the formula:



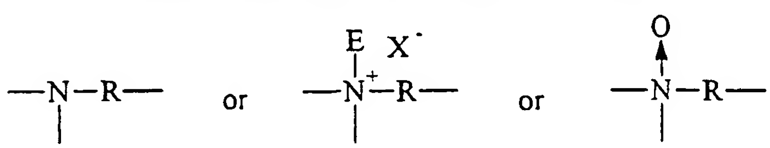
;

ii) W units are backbone units having the formula:



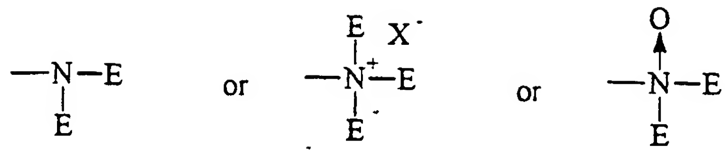
;

iii) Y units are branching units having the formula:



; and

iv) Z units are terminal units having the formula:



;

wherein backbone linking R units are selected from the group consisting of C_2-C_{12} alkylene, C_4-C_{12} alkenylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxy-alkylene, C_8-C_{12} dialkylarylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OR^2)CH_2-$, and mixtures thereof; wherein R^1 is C_2-C_6 alkylene and mixtures thereof; R^2 is hydrogen, $-(R^1O)_xB$, and mixtures thereof; R^3 is C_1-C_{18} alkyl, C_7-C_{12} arylalkyl, C_7-C_{12} alkyl substituted aryl, C_6-C_{12} aryl, and mixtures thereof; R^4 is C_1-C_{12} alkylene, C_4-C_{12} alkenylene, C_8-C_{12} arylalkylene, C_6-C_{10} arylene, and mixtures thereof; R^5 is C_1-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxy-alkylene, C_8-C_{12} dialkylarylene, $-C(O)-$, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, and mixtures thereof; R^6 is C_2-C_{12} alkylene or C_6-C_{12} arylene; E units are selected from the group consisting of hydrogen, C_1-C_{22} alkyl, C_3-C_{22} alkenyl, C_7-C_{22} arylalkyl, C_2-C_{22} hydroxy-alkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_xB$, $-C(O)R^3$, and mixtures thereof; oxide; B is hydrogen, C_1-C_6 alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q-(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to 400; n has the value from 0 to 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1.

2. The process of claim 1 wherein the viscosity of said modified polyamine is from 100 cps to 5000 cps at a temperature of from 4°C to 50°C.

3. The process of claim 1 wherein said particulate carrier is selected from the group consisting of aluminosilicates, phosphates, sulfates, carbonates, silicas and mixtures thereof.

4. The process of claim 1 wherein the mean residence time in said mixer is from 1 second to 20 minutes.

5. The process of claim 1 wherein said particulate carrier is aluminosilicate.

6. The process of claim 1 wherein said particulate carrier is a mixture of sodium carbonate, sodium tripolyphosphate, and aluminosilicate.

7. The process of claim 1 wherein said mixer is a mixer having a central shaft rotating from 200 rpm to 4000 rpm.

8. The process of claim 1 wherein said agglomerating step includes from 20% to 65% by weight of said modified polyamine.

9. The process of claim 1 wherein R is C_2-C_{12} alkylene.

10. An agglomerated detergent admix made according to the process of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/16808

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/00 C11D11/00 C11D3/37 C11D3/12 C11D3/10 C11D3/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 98 08925 A (THE PROCTER & GAMBLE CO.) 5 March 1998 see page 4 - page 8; claims see page 20 - page 24	1-10
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
23 November 1998	02/12/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Serbetsoglou, A

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 108 646 A (BEERSE LISA A. ET AL.) 28 April 1992 cited in the application see claims; examples	1,3-7
A	EP 0 351 937 A (UNILEVER PLC.) 24 January 1990 cited in the application see page 4, line 30 - page 6, line 36 see claims	1,3-7

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